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TIN PLATING METHOD [Suzu mekki hoho]

Kaoru Hirakata et al.

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INVENTORS	(72):	Kaoru Hirakata et al.	
APPLICANT	(71):	Japan Carlit K.K.	
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### Claims

- 1. A tin plating method, characterized in that an electrode comprising a corrosion-resistant metal base having a coating layer consisting of tin oxide, iridium oxide and/or platinum is utilized as the anode when performing tin plating from an acidic tin plating bath by an electroplating method.
- 2. A tin plating method described in Claim 1, characterized in that the tin content in the coated layer consisting of tin oxide, iridium oxide and/or platinum is 3-80 mol%.

## Detailed explanation of the invention

Industrial application field

The present invention relates to a method for performing tin plating from an acidic tin plating solution by electroplating method.

### Prior art

Until recently, a soluble tin anode is utilized when performing tin electroplating from an acidic tin plating solution in the surface treatment in the steel industry, but not only is said tin anode is consumed rapidly and the size stability is poor, the shortcomings also include a high tank voltage and difficult handling of the plating solution.

Thus, insoluble anodes are being utilized in recent years and lead alloy or platinum electroplated-titanium anode (Pt-Ti anode) is the main type for this application. However, the shortcoming for the lead alloy anode is that a large amount of harmful lead is released into the plating solution and the lead is deposited as an alloy on the tin plating film, causing undesirable consequences. Accordingly, more Pt-Ti-type anodes are gradually being utilized.

Problem to be solved by the invention

The high cost of the aforementioned Pt-Ti anode electrodes is the reason for expensive anodes; therefore, development of a tin plating method using low-cost and durable anodes while not polluting the plating solution is very desirable.

### Means to solve the problem

The present inventors have been investigating tin plating method from the aspect of the anode material utilized. We investigated anode electrodes by coating titanium with platinum metal oxides by the thermal decomposition method, but the lifespan of the product was not quite satisfactory because it was only slightly longer than that of the aforementioned Pt-Ti anode electrode, even though the cost was lower compared with that of the Pt-Ti anode electrode. We further investigated other insoluble anodes, and as a result, achieved the present invention.

Specifically, the present invention relates to a tin plating method, characterized in that an electrode comprising a corrosion-resistant metal base having a coated layer consisting of tin oxide, iridium oxide and/or platinum is utilized as the anode when performing tin plating from an acidic tin plating bath by an electroplating method.

An excessive amount of tin oxide in the coated layer consisting of the tin oxide, iridium oxide and/or platinum results in increasing tank voltage; conversely, the lifespan of the electrode is shortened if the amount is too low. Accordingly, the content of the tin oxide is preferably 3-8 mol%, but more preferably 5-70 mol%.

Metals for (light) bulbs such as titanium, niobium, tantalum and zirconium are suitably utilized as the corrosion-resistant metals, but titanium is preferably utilized for its low cost.

A thermal decomposition method, for example, is utilized as the method for coating tin oxide, iridium oxide and/or platinum on the corrosion-resistant metal base material. Specifically, a coating solution prepared by dissolving a tin compound such as stannous chloride, an iridium compound such as iridium chloride and a platinum compound such as chloroplatinic acid in alcohol is coated on a corrosion-resistant metal base material pre-treated by sandblasting or pre-etched with hydrochloric acid or hydrofluoric acid by heating at 400-600°C in an electric oven with an air atmosphere. An electrode coated with tin oxide, iridium oxide and/or platinum can be obtained by repeating said operation several times as necessary.

## Application examples

The present invention is specifically described using the following application examples, but these application examples are not to be construed as limiting the embodiments of the present invention.

### <u>Application Example 1</u>

The surface of a 15 x 200 x 1 mm titanium plate serving as a base material was defatted with trichlene, followed treating with hot oxalic acid to roughen the surface. Chloroiridic acid and stannous chloride were weighed based on Ir:Sn = 3:7 (molar ratio), followed by dissolving in excessive butanol, and the solution was coated on the plate, heated at  $500^{\circ}$ C for 1 h in an electric oven with an air atmosphere, and an electrode having a coated layer comprising iridium oxide and tin oxide was obtained by repeating the operation until the coated content of iridium chloride (converted to iridium) was 6 g/m<sup>2</sup>.

An electroplating test was performed using said electrode as the anode, a titanium plate as the cathode and a 50°C acidic tin plating solution consisting of 25g/L stannous oxide and 80 g/L

phenolsulfonic acid at current density of 30 A/dm<sup>2</sup>. The plating test was terminated after 70 d by estimating the lifespan of the anode from the tank voltage of higher than 10 V.

# **Application Example 2**

The surface of a 15 x 200 x 1 mm titanium plate serving as a base material was sandblasted. Chloroiridic acid, stannous chloride and chloroplatinic acid were weighed based on Ir:Sn:Pt = 4:4:2 (molar ratio), followed by dissolving in excess ethanol, and the solution was coated on the plate, heated at  $500^{\circ}$ C for 20 min in an electric oven with an air atmosphere, and an electrode having a coated layer comprising iridium oxide and platinum was obtained by repeating the operation until the coated content of iridium chloride (converted to iridium) was  $9 \text{ g/m}^2$ .

An electroplating test was performed under the same conditions as in Application Example 1, using said electrode as the anode. The plating test was terminated after 75 d by estimating the lifespan of the anode from the tank voltage of higher than 10 V.

## Application Example 3

The surface of a 15 x 200 x 1 mm titanium plate serving as a base material was etched with hot concentrated hydrochloric acid. A coating solution of Ir:Sn:Pt = 7:1:2 (molar ratio) was prepared by the same method as in Application Example 2, coated on the base material by heating at  $500^{\circ}$ C for 1 h in an electric oven with an air atmosphere, and an electrode having a coated layer comprising iridium oxide, tin oxide and platinum was obtained by repeating the operation until the coated content of iridium chloride (converted to iridium) was  $14 \text{ g/m}^2$ .

An electroplating test was performed under the same conditions as in Application Example 1, using said electrode as the anode. The plating test was terminated after 79 d by estimating the lifespan of the anode from the [illegible] voltage of higher than 10 V.

# Application Example 4

The surface of a 15 x 200 x 1 mm titanium plate serving as a base material was etched with hot oxalic acid. Stannous chloride and chloroplatinic acid were weighed based on Sn:Pt= 3:7 (molar ratio), followed by dissolving in a suitable amount of amyl alcohol, and the solution was coated on the plate by heating at  $500^{\circ}$ C for 20 min in an electric oven with air atmosphere, and an electrode having a coated layer comprising tin oxide and platinum was obtained by repeating the operation until the coated content of iridium chloride (converted to iridium) was  $14 \text{ g/m}^2$ .

An electroplating test was performed under the same conditions as in Application Example 1, using said electrode as the anode. The plating test was terminated after 71 d by estimating the lifespan of the anode from the tank voltage of higher than 10 V.

## Comparative Example 1

An electroplating test was performed under the same conditions as in Application Example 1, using a commercial Pt-Ti electrode (3.5 µm platinum coated thickness) of the same size as in Application Example 1. The plating test was terminated after 18 d by estimating the lifespan of the anode from the tank voltage of higher than 10 V.

# Comparative Example 2

An electroplating test was performed under the same conditions as in Application Example 1, using a commercial IrO2-Ti electrode (20 g/m<sup>2</sup> IrO2) of the same size as in Application Example 1. The plating test was terminated after 25 d by estimating the lifespan of the anode from the tank voltage of higher than 10 V.

# Effect of the invention

The tin plating method of the present invention utilizes anodes of low cost and it can be utilized in plating for a long time without polluting the plating solution because the anodes exhibit excellent durability in the tin plating solution.